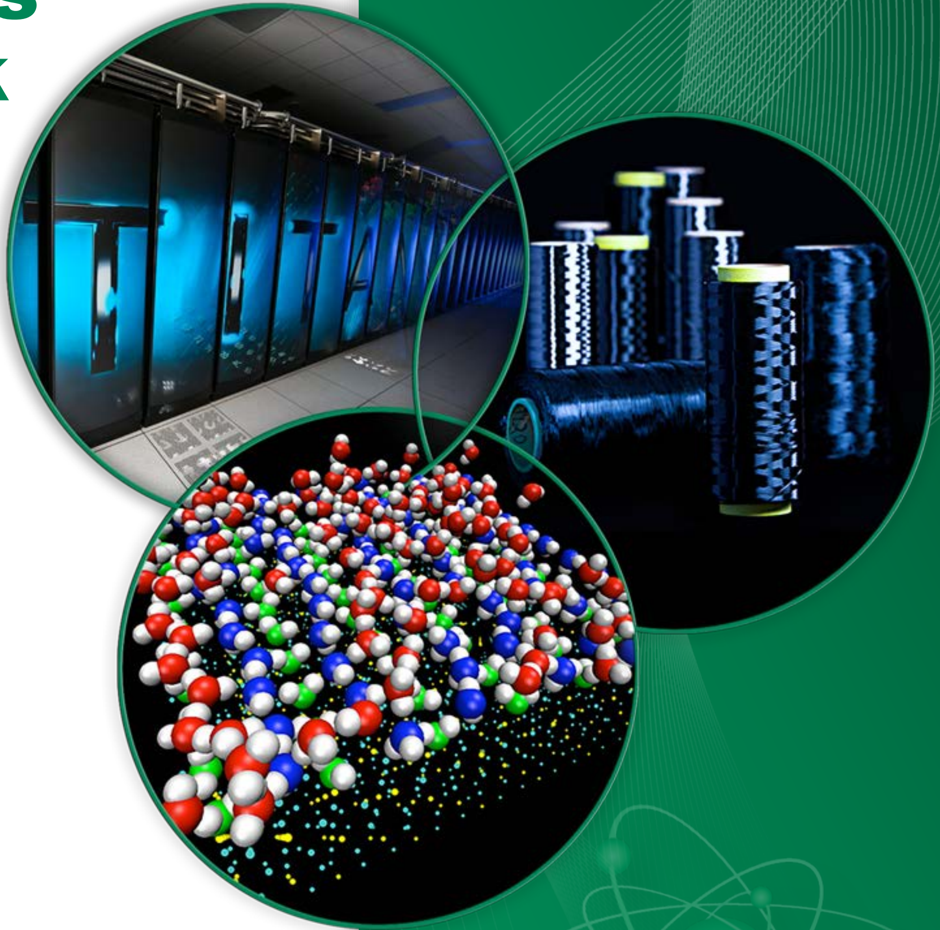
Towards Solventless Processing of Thick Electron-Beam (EB) Cured Lithium-Ion Battery Cathodes



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June 8, 2017

ES207

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Overview

Timeline

- Task Start: 10/1/14
- Task End: 9/30/19
- Percent Complete: 45%

Barriers

- Barriers addressed
  - By 2022, further reduce EV battery cost to \$125/kWh.
  - Materials processing cost reduction and electrode thickness increase of ≥2×.
  - Achieve deep discharge cycling target of 1000 cycles for EVs (2022).

Budget

- Total task funding
  - \$1425k
- \$125k in FY15
- \$150k in FY16
- \$350k in FY17

Partners

- Interactions/Collaborations
  - Equipment Suppliers: ebeam Technologies, Keyland Polymer, NEO Beam.
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Materials Suppliers: TODA America, Allnex, Keyland Polymer, Alabama Graphite.
- Project Lead: ORNL

Objectives & Relevance

- **Main Objective: To achieve 1) significant process energy savings; 2) ultra-high electrode processing speed; and 3) utilize much more compact equipment than conventional drying ovens.**
  - EB treatment is a fast, robust materials processing technology.
  - Low cost and excellent compatibility with high-volume materials production.
  - Unmatched throughput: ≥600 m^2/min throughput can be achieved based on ≥300 m/min line speed for roll widths up to 2 m ($1.5-2.0M installed with footprint ~10 m^2).
  - Thicker electrodes: It is expected that cathode coatings of **several hundred microns** can be processed at ~150 m/min or with a larger equipment footprint.
  - Excellent energy efficiency – Electrical efficiencies ≥60% are possible.
  - Environmentally friendly – EB processing requires no solvent and no photoinitiator and has low emissions.

- **Relevance to Barriers and Targets**
  - *Significantly enabling technology for achieving ultimate EV battery pack cost of $125/kWh through substantial materials processing cost reduction.*
  - *Further enables cell energy density improvement through electrode thickness increases of at least 2×.*
  - *Develops deposition methods for electrode manufacturing requiring little or no solvent.*

Task Milestones and progress

Status	SMART Milestones	Description
6/30/17 **On track**	FY17 Milestone	Demonstrate no more than 20% capacity fade through 300 cycles at 0.33C/-0.33C in 1.5 Ah pouch cells with optimized cathode EB curing formulation and areal loading of 25 mg/cm^2 at a curing speed of 150-200 m/min; complete pouch cell rate performance from C/20 to 1C.
6/30/17 **On track**	**Go/No-Go Decision**	Cathode EB Curing Speed and Areal Loading Demonstration – Demonstrate 25 mg/cm^2 NMC 532 cathode coating areal weight with full EB cure and down-selected electrode formulation with selected industrial partner at 150-200 m/min. Criteria: If this outcome is a no-go, then either the EB formulation will be redesigned, the industrial partner production process will be modified (nitrogen blanket, etc.), or both for FY18.

Approach

- **Major problems to be addressed:**
  - Conventional solvent primary drying ovens for lithium-ion electrodes are not compatible with high line speeds or must include long drying lines to accommodate high line speeds.
  - These drying lines are capital intensive and require a large amount of battery plant space.
  - Cost of organic solvents and solvent handling are prohibitive in terms of processing cost and capital expense.
- **Overall technical approach and strategy:**
  1. Phase 1 – Demonstrate the technology's key differentiating attributes of high throughput and thick layer processing (FY15-16).
  2. Phase 2 – Address the key challenges of EB curing parameters and resulting material performance; develop coating methods requiring little or no solvent. (FY17-18).
  3. Phase 3 – Demonstrate an optimized curing system in conjunction with a high-speed coating line together with a key equipment partner and battery manufacturer (FY19).

Technical Accomplishments – Executive Summary

Address the key challenges of high speed EB curing parameters;

Trouble shooting for the first high speed EB curing trial run: poor adhesion from O_2 inhabitation and poor coating quality .

Successful curing demonstrated at 150 m/min line speed with low O_2 level and good coating adhesion observed.

Develop coating methods requiring little or no solvent.

First round of spraying coating was evaluated. Resin size needs to be reduce for good distribution of resin in the system.

Second round of spraying coating was evaluated. Good materials distribution and adhesion after calendering was observed.

High Speed Demonstration I: Trouble-Shooting on Poor Adhesion

- EB curing line speed demonstrations were conducted at ebeam technologies.
  - Tunable energy from 100 to 300 keV
  - Line speed up to 650 fpm
- Experimental runs in FY16 showed poor adhesion of coating.
  - Curing conditions: 275 keV, 30 KGy, 450 fpm, >1000 ppm O_2.
  - Poor adhesion was noticed for the high speed curing due to oxygen inhibition as shown below.

Fig. 1. photos of cured coating with bad adhesion

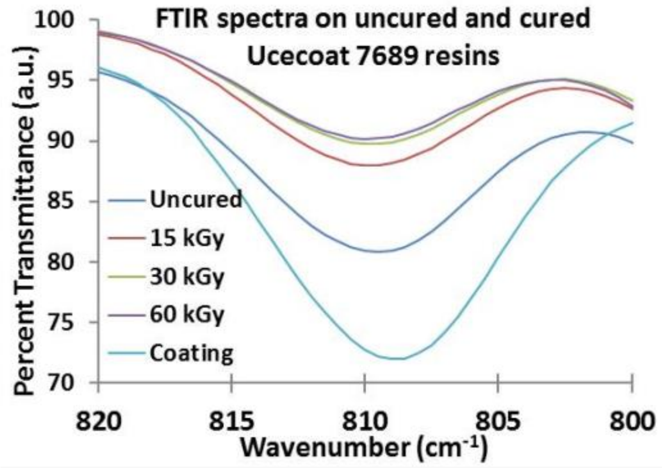


Fig. 2. FTIR showing the resin in the coating is not cured at high speed trial run.

Strong Propagating radical

Weak Propagating radical

$$R\bullet + O_2 \rightarrow R-O-O\bullet$$

Oxygen scavenging reaction

Strategies for Improvement in High Speed EB Curing Demonstration II

- Formulation is improved to obtain crack-free, thick coatings.
- Calendering before curing to lower the porosity and reduce trapped air in pores.
- Nitrogen purge in the curing chamber is improved to reduce O_2 level.
- Dose is increased to get more electrons (more free radicals) to offset the O_2 inhibition.

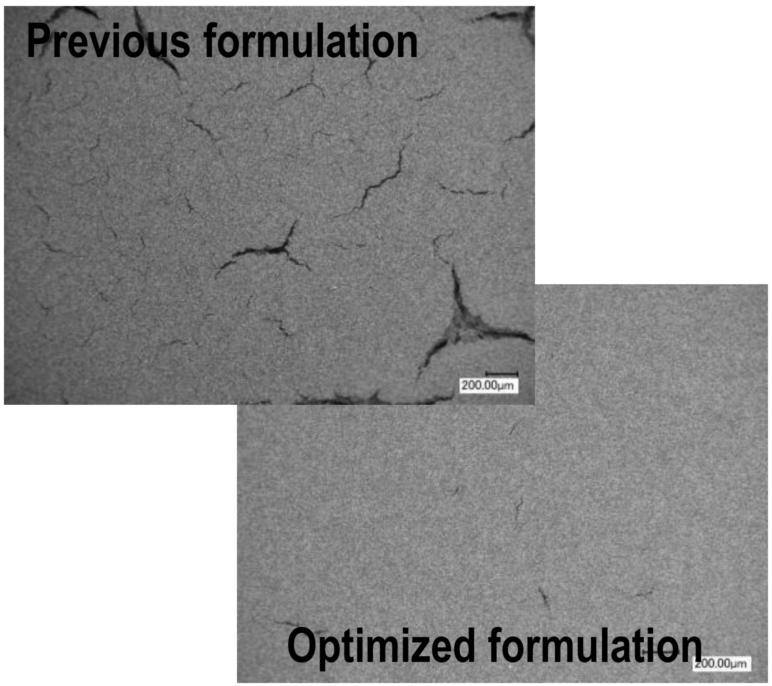


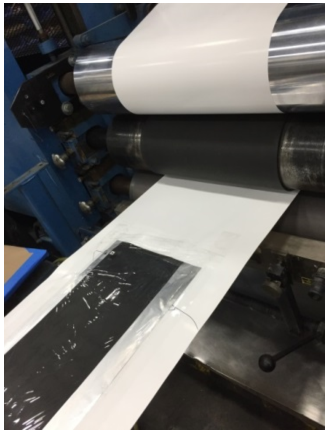
Figure 1. coating quality improvement due to formulation optimization.

Figure 2. porosity reduction using calendering process.

Zhijia Du, et al, “Enabling aqueous processing for crack-free electrodes”, *J. Power Sources*, In Press

High Speed Demonstration II: Minimize O_2 Level in Curing Process

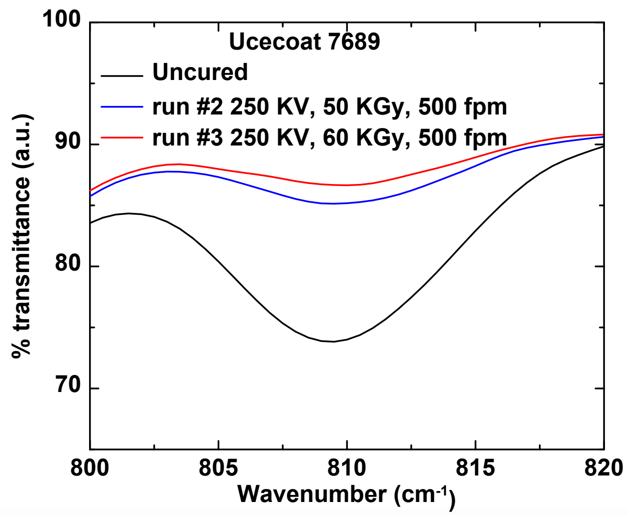
Run No.	Sample Name	Experimental details	EB conditions kV/kGy/fpm
1	1A	with no film;	275/60/300 300 ppm O_2
	1B	covered and N_2 inerted using biax nylon film;	
	1C	covered and N_2 inerted using Stretch-tite film.	
2	2A	with no film;	250/50/500 560 ppm O_2
	2B	covered and N_2 inerted using Stretch-tite film;	
	2resin	uncovered dry Ucecoat 7788 & 7689 resin.	
3	3A	with no film	250/60/500 300 ppm O_2
	3B	covered and N_2 inerted using biax nylon film;	
	3C	covered and N_2 inerted using Stretch-tite film.	
	3resin	uncovered dry Ucecoat 7788 & 7689 resin	

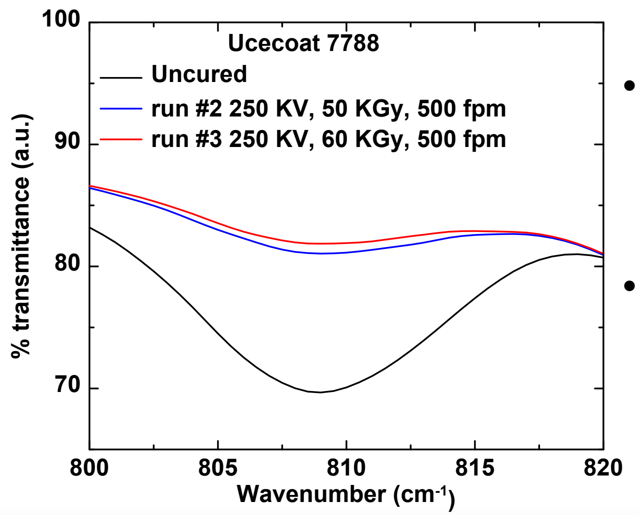


- Coating were taped on periphery to paper leader and filled with N_2.
- High line speed of 300-500 fpm was demonstrated with reduced O_2 level of 300 ppm.
- The EB curing at 500 fpm is using the upper limit of the pilot line at 60 kGy and 250 kV.

Dosimeters and FTIR Confirmed the Penetration and Curing of Resins

Trial no.	Sample No	Conditions	Dose (kGy)		
			Top	Bottom	Bottom w/o Al foil
#1: 60 kGy, 275 keV, 300 fpm, 300 ppm O_2	1A	No Film	61.1	34.7	43
	1B	Stretch-tite	61.4	36.7	46
	1C	Nylon	52.9	39.6	45
#2: 50 kGy, 250 keV, 500 fpm, 560 ppm O_2	2A	No Film	50.3	22.9	30
	2B	Stretch-tite	52.3	23.9	31
#3: 60 kGy, 250 keV, 500 fpm, 300 ppm O_2	3A	No Film	65.6	29.3	40
	3B	Stretch-tite	67	28.7	40
	3C	Nylon	66.5	29	40

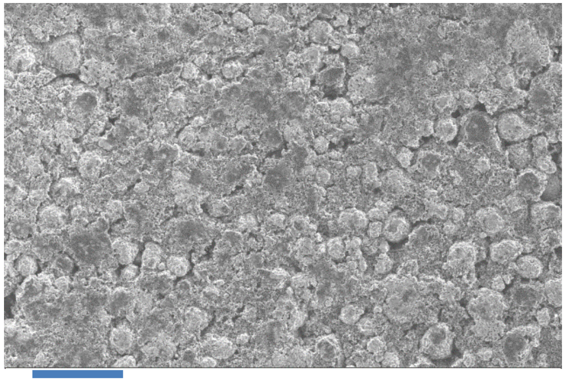




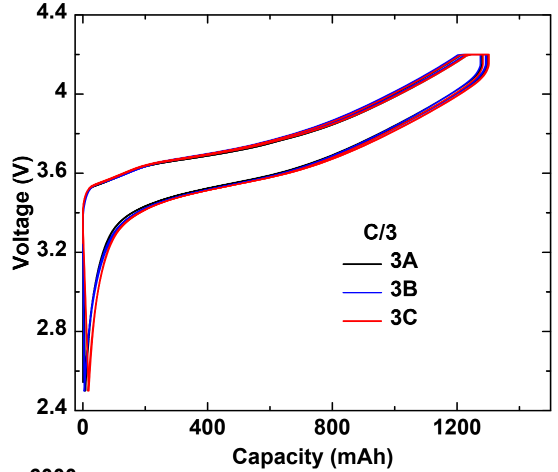
- Higher voltage for run #1 has higher penetration of dose compared to lower voltage curing run #2 & 3.
- FTIR of pure resins after EB curing run #2 and #3 confirmed the cross-linking of C=C in the resin.

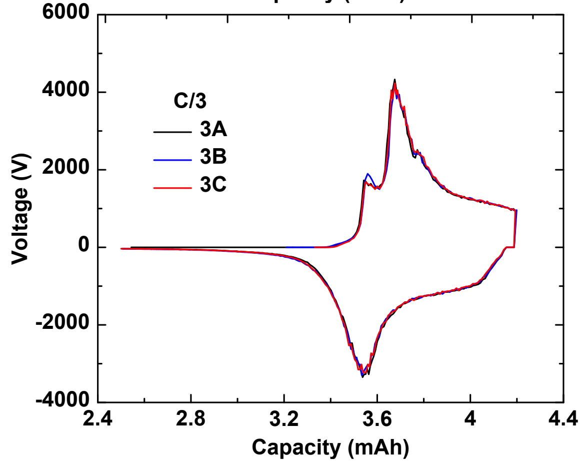
EB Cured Electrodes Show Good Rate Performance

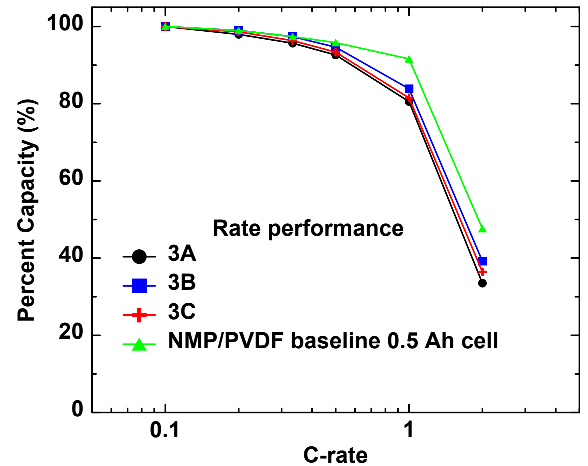
1.5 Ah pouch cell demonstration on run #3 (500 fpm).

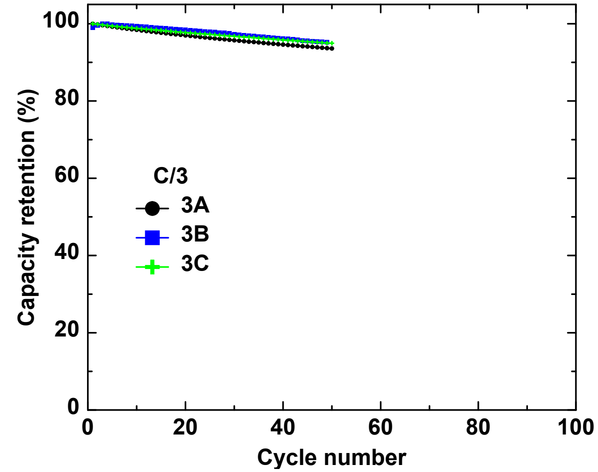


SEM images showing the morphology of the electrode.







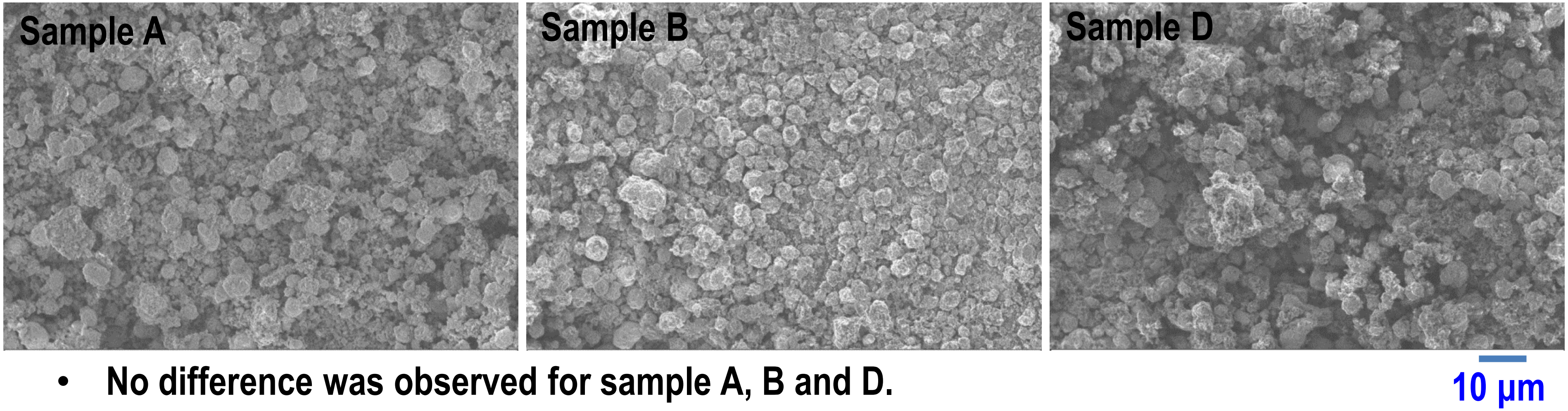


- 1.5 Ah cells has typical NMC532 charge/discharge curves.
- Good rate performance was achieved from C/10 to 2C.
- C/3 cycling performance is under testing and up to 50 cycles (4/24/17).

Development of Solvent-less Coating Method

- 5 dry powders were prepared with formulation of NMC/CB/Resin 87/5/8 wt%.
- Sample BCDE were prepared from slurry and then dried.
- Sample A: the resin is 40 wt% in water. The materials were mixed, ground and dried.

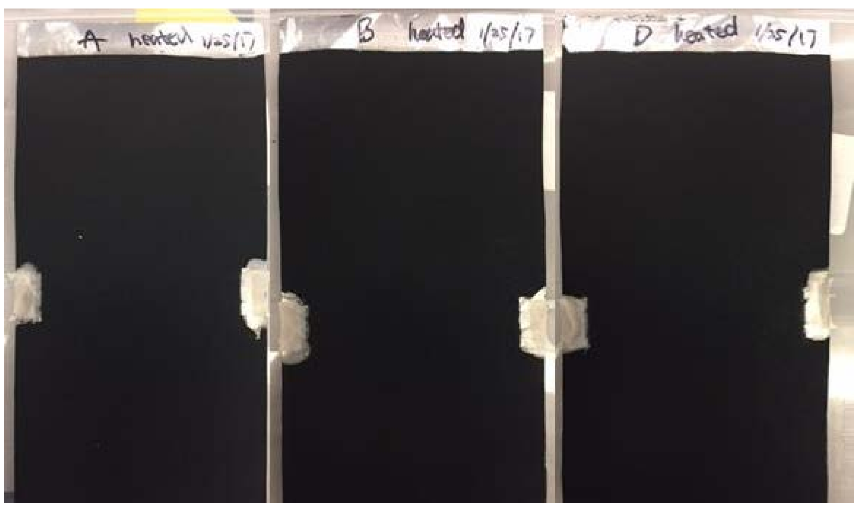
Sample	Resin	Photoinitiator	Solvent	Note
A	Ucecoat A	N	No water	EB curing
B	Ucecoat A	N	water	EB curing
C	Ucecoat A	Y	water	UV curing Keyland
D	KP-B	N	Acetone	EB curing
E	KP-B	Y	Acetone	UV curing Keyland



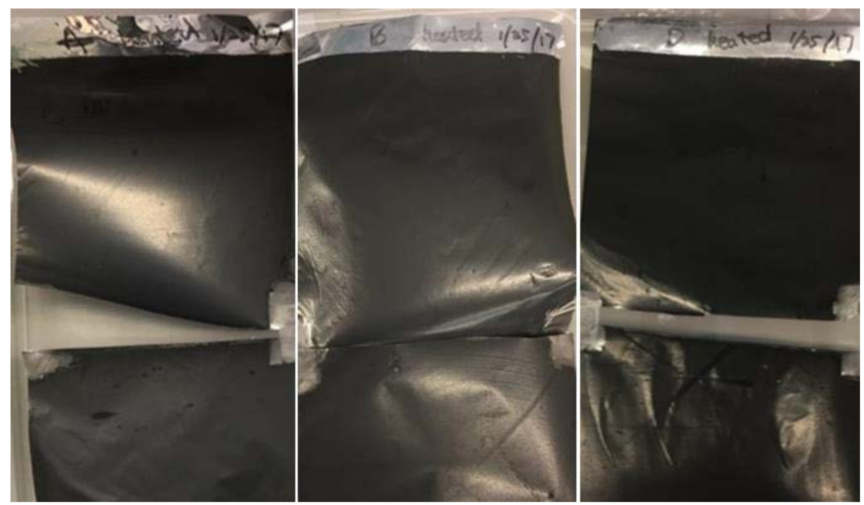
- **No difference was observed for sample A, B and D.**
- **Binder was well dispersed in the NMC and carbon black mixtures.**

Successful Demonstration of Electrostatic Spraying at Keyland Polymer

Collaborators at Keyland Polymer are evaluating electrostatic spraying method for battery coatings.

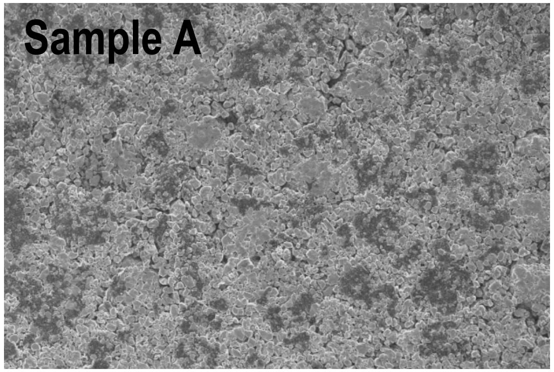


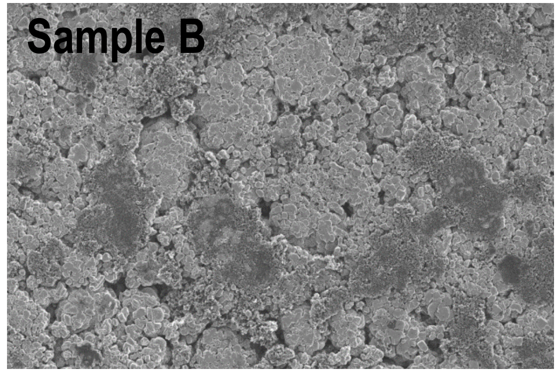
All the powders were well attached to the substrate after electrostatic spraying.

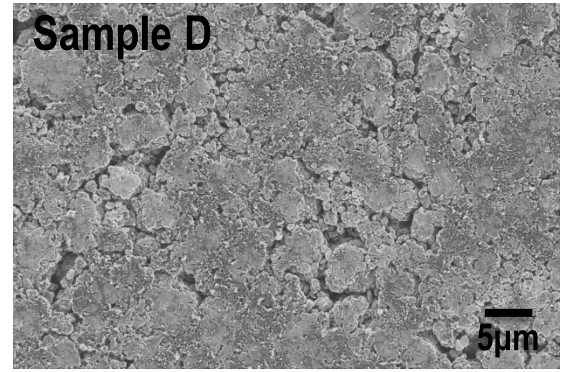


All the samples were calendared and adhesion was improved.

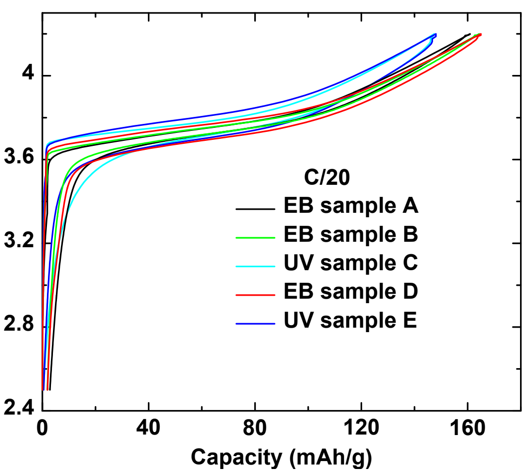
Morphologies and Performance of EB/UV cured samples

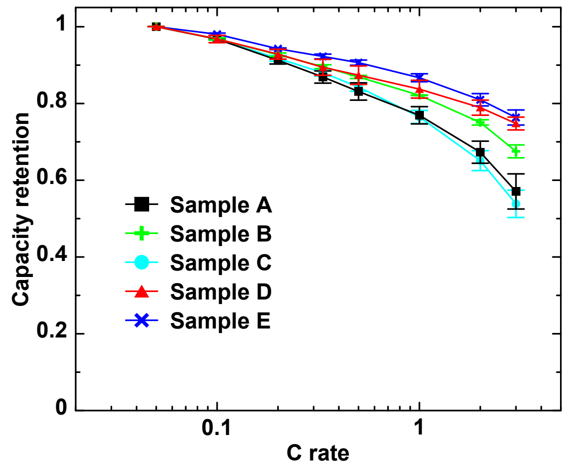


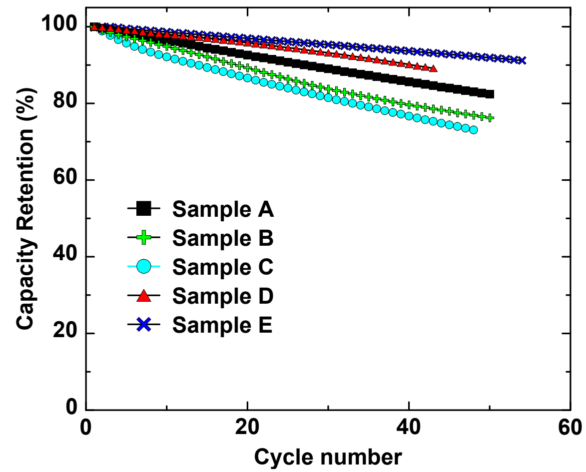




- Sample A has better dispersion of carbon black than sample B due to using balls in mixing.
- Sample D also has good dispersion of carbon black due to the use of acetone as solvent.







The sprayed and cured samples show typical NMC532 lithium intercalation/de-intercalation behavior. Sample D and E has slightly better rate and cycling performance.

Proposed Future Research

- **High speed EB curing demonstration**
  - Continue evaluation of high speed cured coating on electrochemical performance.
- **Binder evaluation for spraying powder coating**
  - Resin size reduction using jet mill to break resin particle size to 0.3-0.5 mircons.
  - Evaluation of different mixing methods such as high shear mixing to get better resin distribution in the dry powder.
  - Continuing binder optimization including different type of resins and different content ratio in formulation.
- **Thick electrode using electrostatic spraying methods**
  - Thick coating (25 mg/cm^2) with optimized binder distribution, porosity control, mechanical integrity.
  - Analysis/validation of production speed, cost reduction of the combination of spraying and EB curing.
- ***Other manufacturing methods compatible with high speed production such as gravure coating, metering rod (meyer rod) coating, etc.***

Any proposed future work is subject to change based on funding levels.

Collaborations

- Partners
  - Equipment Suppliers: ebeam Technologies, Keyland Polymer, B&W MEGTEC, Eastman Kodak
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Raw Materials Suppliers: TODA America, Keyland Polymer, Alabama Graphite

- Collaborative Activities
  - Extensive EB and UV curing trials were completed at Keyland Polymers, NEO Beam and ebeam Technologies lab-scale unit in 2016 and 2017.
  - High speed curing at 500 fpm are currently being scaled to ebeam Technologies pilot coating and curing line in Davenport, IA.
  - Powder coating is currently being evaluated in lab scale at Keyland Polymers.

Summary

- **Objective:** To achieve 1) significant process energy savings; 2) ultra-high electrode processing speed; and 3) utilize much more compact production equipment.
- **Approach:** Three-phase approach from formulation chemistry to full-scale production.
  1. Phase 1 – Demonstrate the technology's key differentiating attributes of high throughput and thick layer processing (FY15-16).
  2. Phase 2 – Address the key challenges of EB curing parameters and resulting material performance; develop coating method that require little or no solvent. (FY17-18).
  3. Phase 3 – Demonstrate an optimized curing system in conjunction with a high-speed coating line together with a key equipment partner and battery manufacturer (FY19).
- **Technical:** *150 m/min EB curing pilot line demonstration, 1.5 Ah pouch cell performance evaluation, dry powder mixing evaluation, and electrostatic spraying of powder coating with good electrochemical performance*.
- **Collaborators:** High speed curing trials are currently being scaled up at ebeam technologies pilot line in Davenport, IA. Electrostatic spraying powder coating are currently being evaluated at Keyland Polymer in Cleveland, OH. Plans to investigate other high-speed coating with high solids (low solvent) content with either B&W MEGTEC or Eastman.
- **Commercialization:** High likelihood of technology transfer because of strong industrial collaboration, significant electrode production cost reduction, and impact on cell energy density (≥2× thicker cathodes).

Selected Responses to Specific FY16 DOE AMR Reviewer Comments

Reviewer 1: The development of a high-speed curing process begets challenges in the development of a high-speed coating process for the very viscous starting material.

- ✓ *We have realized that this is a challenging projects and we have outlined the development roadmap for a compatible coating and curing process. We have been discussing with coating experts about several different coating processes such as gravure, metering-rod, extrusion, spraying, etc. Currently, we are developing spraying coating methods for the EB curing process*

Reviewer 2: The reviewer said it is not very clear what the contribution is of the individual barriers identified to the cost savings. If established, it would be easier to prioritize and maintain focus.

- ✓ *The cost contribution we calculated in FY16 is based on the high speed curing process in this project versus thermal drying process in the industry. $0.056/kWh processing cost has been estimated in high volume. This high cost-saving feature is the driving force to continue the high speed EB curing evaluation on electrochemical performance. We are currently evaluating the compatible high speed coating methods and their relevant cost savings compared to slot-die coating method.*

Reviewer 1: Resources were sufficient for perhaps developing the drying/curing portion of the program, and perhaps under-resourced if expanded into high-speed deposition of high-viscosity coatings.

- ✓ *We have reached out to the industry for possible coating method development and We are currently working with Keyland Polymer for the development of powder coatings.*

Acknowledgements

- U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (Deputy Director: David Howell and Program Manager: Peter Faguy)

- ORNL Contributors:
  - Rose Ruther
  - Marrisa Wood
  - TJ Christensen
  - Jesse Andrews

Technical Collaborators

- Michael Knoblauch
- Tony Carignano
- Sage Schissel
- Michael Bielmann
- Jeff Quass
- Dave Ventola
- Kevin Dahlberg
- Mike Wixom
- Dan Occorr
- Jesse Edmondson

Information Dissemination and Commercialization

Refereed Journal Papers and Presentations

- Z. Du, C.J. Janke, J. Li, C. Daniel, and D. L. Wood III, “Electron beam curable acrylated polyurethanes as novel binders of Li-ion battery electrodes” *J. Electrochem. Soc.*, 163 (2016): A2776-A2780.
- Zhijia Du, David Wood, Claus Daniel, Sergiy Kalnaus, and Jianlin Li, “Understanding limiting factors in thick electrodes towards high energy density Li-ion batteries”, *J Applied Electrochem*, 47 (2017) 405-415.
- Zhijia Du, K. Rollag, J. Li, S. J. An, M. Wood, Y. Sheng, P. Mukherjee, C. Daniel, and D.L. Wood, “Enabling aqueous processing for crack-free electrodes”, *J Power Sources*, In Press.
- Jianlin Li, Zhijia Du, et. al., “Towards low-cost, high energy density and high power density lithium-ion batteries” *JOM*, under review. (Invited Paper)
- Z. Du, C. J. Janke, C. Daniel, J. Li, and DL Wood III. "Electron beam curing of acrylated polyurethanes and associated applications in Li-ion batteries." The 18th International Coating Science and Technology Symposium, September 18-21, 2016, Pittsburgh, PA.

Thank you for your attention!

Back-up Slides

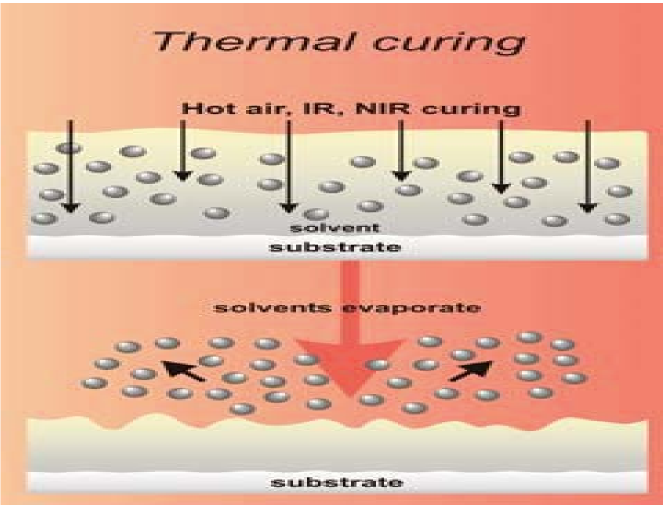
Advantage of Chemical Curing over Physical Drying

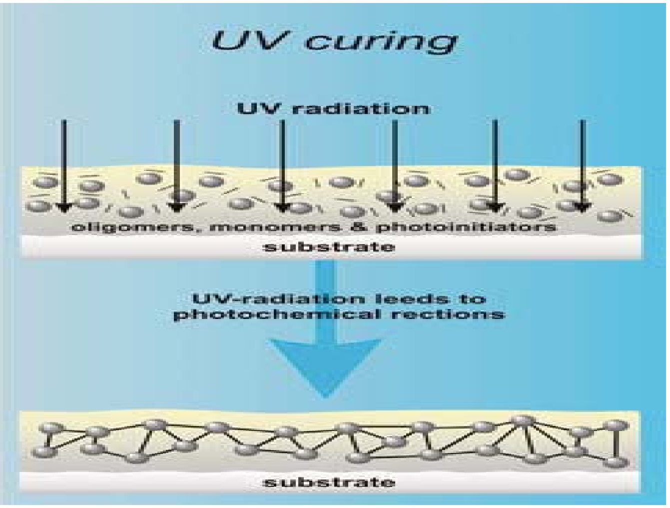
Physical drying

- Solvent evaporation
- Physical drying
- No crosslinking
- High MW polymers

Radiation curing

- No VOC emission (Ultimate goal)
- Radiation-induced polymerization & crosslinking
- Crosslinking to produce a rigid network
- Low MW oligomers→high MW polymers



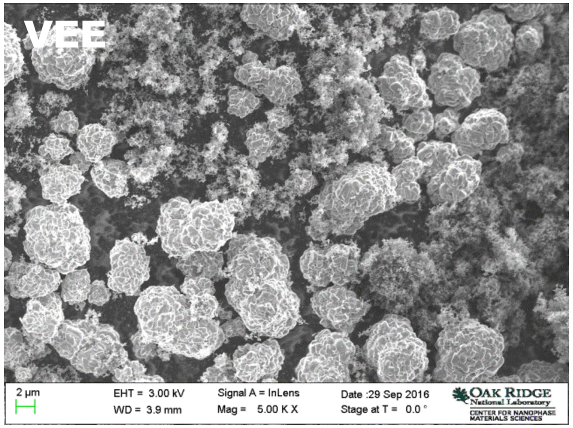


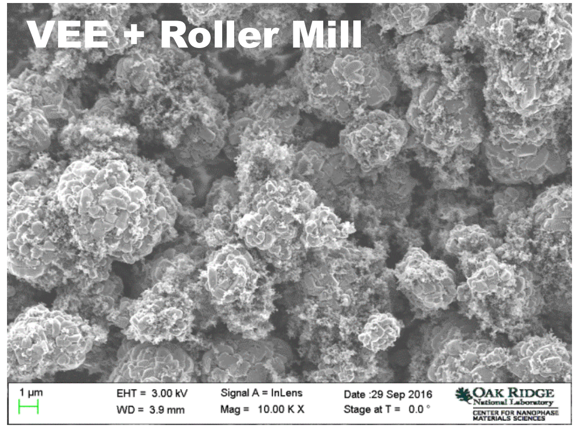
- Significant process energy savings
- Ultra-high speed
- Utilizes much more compact equipment than conventional drying ovens.

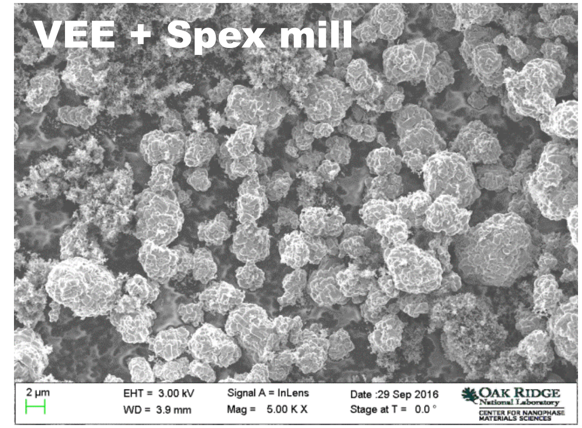
The transformation from liquid to solid is extremely fast (<1second)

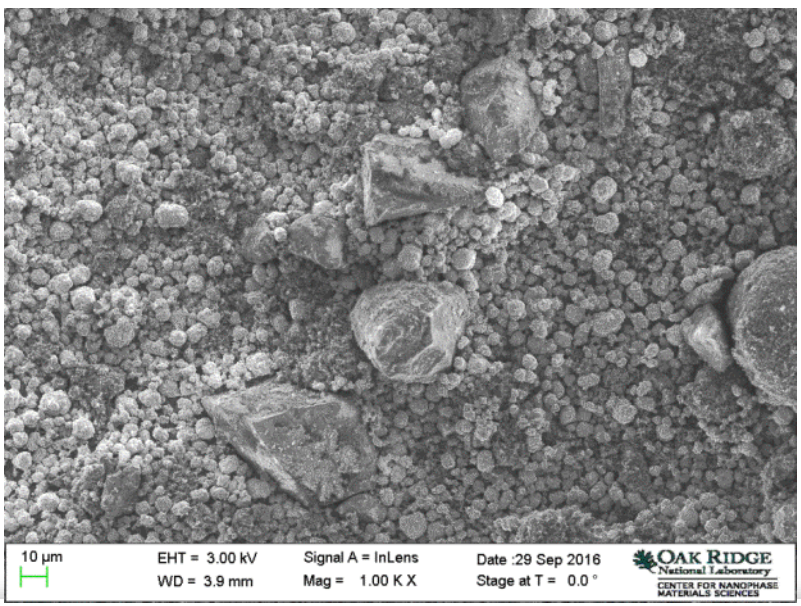
http://www.honleuv.com/news/2014/5/28/fundamental-principles-of-uv-reactive-manufacturing-processe.html

Dry Powder Mixing



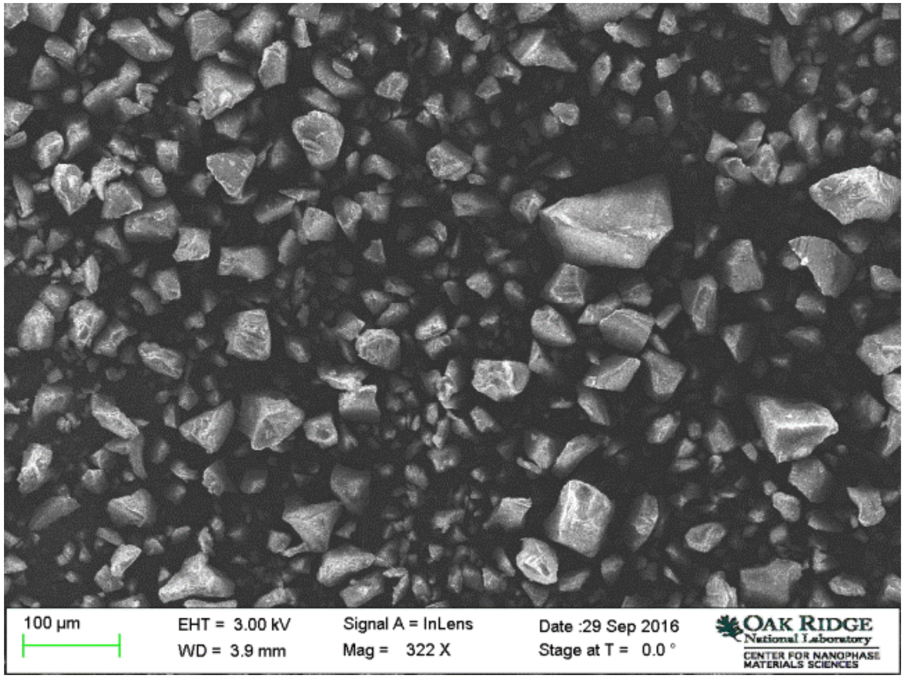


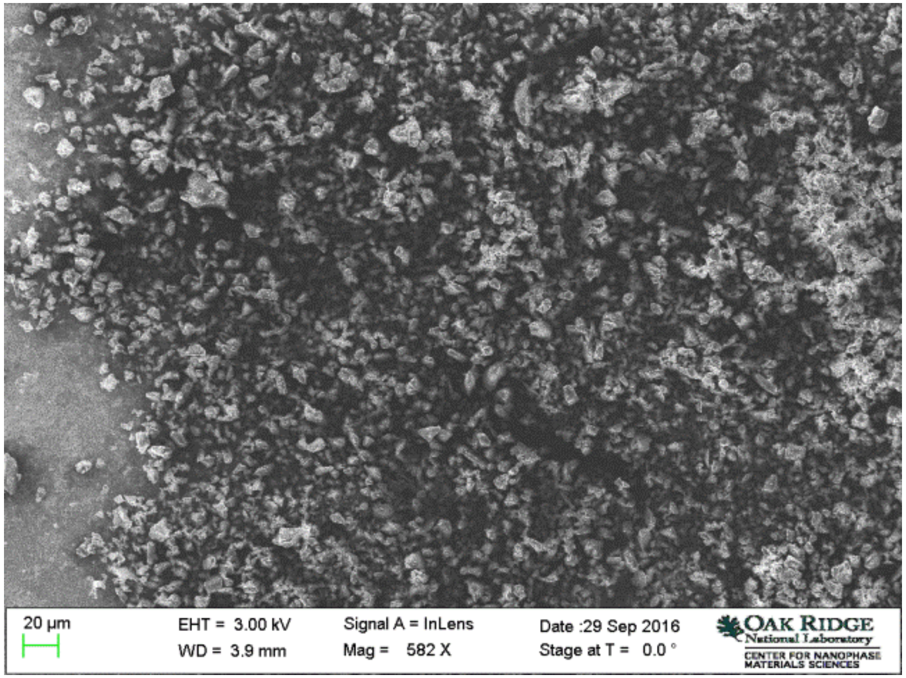




Those giant particles are the resins (acrylated polyester), which could NOT disperse uniformly in the coating.

Cryogenic Grinding of Polymer Powder





30-40 µm

< 10 µm after 1 hr grinding

Producing resins with smaller particle size is currently being evaluated for jet mill method.